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METHOD OF PRODUCING A PERFLUOROCARBON POLYMER HAVING A SULFONIC ACID TYPE FUNCTIONAL GROUP

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METHOD OF PRODUCING A PERFLUOROCARBON POLYMER HAVING A SULFONIC ACID TYPE FUNCTIONAL GROUP

[*Suruhon'san'gata kan'nohki o yuhsuru pahfuruorokahbon jyuhgohtai o seizohsuru hohhoh*]

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[There are no amendments to this patent.]

Specification

1. Title of the invention

Method of producing a perfluorocarbon polymer having a sulfonic acid type functional group

2. Claims of the invention

(1) A method wherein emulsion copolymerization is carried out for a perfluorocarbon monomer having a sulfonic acid type functional group and a perfluoro-olefin in an aqueous medium in the presence of a polymerization initiator, which method of producing a perfluorocarbon polymer having a sulfonic acid type functional group is characterized by the fact that emulsion copolymerization is carried out after emulsification is performed in an aqueous medium in the presence of a fluorine-containing emulsifier for a perfluorocarbon monomer

having a sulfonic acid type functional group by a homogenizer to produce a perfluorocarbon polymer copolymerized with a high proportion of the above-mentioned perfluorocarbon monomer having a sulfonic acid type functional group.

(2) The method of manufacturing described in claim 1 in which the perfluorocarbon monomer having a sulfonic acid type functional group is

$CF_2=CFOCF_2CF(CF_3)O(CF_2)_2SO_2F$

and the perfluoro-olefin is tetrafluoroethylene and the copolymerization ratio of the former is at least 20 wt%.

3. Detailed description of the invention

The present invention pertains to a method of producing a perfluorocarbon polymer having a sulfonic acid type functional group, and the invention further pertains to a new method capable of producing a sulfonic acid type perfluorocarbon polymer having a high sulfonic acid type monomer content, that is, a high ion-exchange capacity, produced upon performing emulsion copolymerization in an aqueous medium.

In the past, a polymerization system that utilizes a perfluorocarboxylic acid type emulsifier such as $C\text{-}F_{16}COONH_4$ and $C_8F_{17}COONH$ is used for emulsion polymerization of a fluorine-containing monomers such as tetrafluoroethylene in an aqueous medium. For copolymerization of a monomer having a carboxylic acid type functional group such as $CF_2=CFO(CF_2)_3COOCH_3$ and C_2F_4, a similar perfluorocarboxylic acid type emulsifier is used, and perfluorocarbon polymer with a high ion-exchange capacity is smoothly and efficiently produced by means of emulsion copolymerization in an aqueous medium.

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On the other hand, in order to achieve high ion-exchange capacity in copolymerization of a monomer having a sulfonic acid type monomer such as

$$CF_2{=}CFOCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FOCF_2CF_2SO_2F$$

and C_2F_4, etc., a solid polymerization method where a polymerization medium is not used or a solution polymerization method where a fluorine type solvent such as trichlorotrifluoroethane is used as a medium can be used. A method where emulsion polymerization is carried out in an aqueous medium for copolymerization of a sulfonic acid type monomer and C_2F_4, etc. is known. However, according to a study done by the present inventors, only materials with a very low ion-exchange capacity can be produced in a standard emulsion polymerization that utilizes a conventional sulfonic acid type emulsifier with the exception of the case where an ultrasonic wave emulsification treatment is provided (see Japanese Kokai [Unexamined] Patent Application No. Sho 60-250009 for reference), and a film capable of achieving 0.5 milliequivalents/gram of dry resin used as a cationic ion-exchange film material is not possible.

Based on the above background, and as a result of much research conducted by the present inventors in an effort to produce a sulfonic acid type perfluorocarbon polymer having high ion-exchange capacity based on emulsion copolymerization in an aqueous medium, interesting factors described below were discovered.

Thus, it was new discovered that the production of a sulfonic acid type perfluorocarbon polymer with a high ion-exchange capacity can be smoothly and efficiently achieved when a fluorine-containing emulsifier is used and an emulsion copolymerization is carried out after emurlsification is performed in an aqueous medium in the presence of a fluorine-containing emulsifier for a perfluorocarbon monomer having a sulfonic acid type functional group by a homogenizer to produce a perfluorocarbon polymer copolymerized with a high proportion of the above-mentioned perfluorocarbon monomer having a sulfonic acid type functional group. In other words, the present invention is a method of producing a perfluorocarbon polymer having a sulfonic acid type functional group characterized by the fact that an emulsion copolymerization is

carried out after emulsification in an aqueous medium in the presence of a fluorine-containing emulsifier for a perfluorocarbon monomer having a sulfonic acid type functional group by a homogenizer so as to produce a perfluorocarbon polymer copolymerized with a high proportion of the above-mentioned perfluorocarbon monomer having a sulfonic acid type functional group in a method where emulsion copolymerization is carried out for a perfluorocarbon monomer having a sulfonic acid type functional group and perfluoro-olefin in an aqueous medium in the presence of a polymerization initiator.

For the homogenizer used in the present invention, a variety of homogenization techniques such as a homogenizer and colloid mill mixer can be used, and those with a high emulsification performance are especially suitable from the standpoint of an increase in the copolymerization ratio of the perfluorocarbon monomer having a sulfonic acid type functional group. In this case, it is desirable when the oil droplets of perfluorocarbon monomer having a sulfonic acid type functional group included in the aqueous medium after the emulsification treatment are 20 μ or less, preferably 5 μ or less, and especially, 2 μ or less for an increase in the copolymerization ratio of the perfluorocarbon monomer having a sulfonic acid type functional group and polymerization treatment with good reproducibility. When emulsification is not adequate, separation of a portion of the monomer from the aqueous medium occurs, at times, but polymerization is possible.

The particle diameter of the dispersed monomer droplets can be measured by a light transmitting decanter type particle diameter distribution meter, AUTOMATIC PARTICLE ANALYZER PA101 (product of Union Research). In this case, the particle diameter of the monomer droplets are determined according to the mean particle diameter based on the area ratio.

It is important to use a fluorine-containing emulsifier and a homogenizer to perform emulsification of the perfluorocarbon monomer having a sulfonic acid type functional group in an aqueous medium in the present invention. After the above-mentioned emulsification is

carried out, emulsion copolymerization is carried out with tetrafluoroethylene and other optional monomers. As for the fluorine-containing emulsifier used in this case, perfluorocarboxylic acid type emulsifiers commonly used for emulsion polymerization of tetrafluoroethylene and other fluorine-containing monomers can be used in this case as well without any restrictions.

For example, a surfactant compound such as an ammonium salt, potassium salt, or sodium salt of a carboxylic acid or sulfonic acid containing a perfluoroalkyl group can be mentioned, and furthermore, surfactant compounds made of compounds containing other perfluoropolyether chains can be mentioned. In general, the above-mentioned fluorine-containing emulsifier is used at a concentration of 0.001 to 5 wt%, preferably 0.05 to 2.0 wt%.

In emulsification of a perfluorocarbon monomer having a sulfonic acid type functional group in an aqueous medium, the above-mentioned fluorine-containing emulsifiers are added. Furthermore, a variety of additives such as commonly-added buffers and molecular weight modifiers may be added before or after the emulsification treatment. The other conditions used for emulsification treatment are not especially limited, and for the temperature used, for example, a temperature in the range of 5 to 90°C can be mentioned.

When the emulsification treatment used in the present invention is used, it is possible to effectively disperse a monomer containing a sulfonic acid type functional group with a very low solubility in an aqueous medium, and as a result, a significant increase in the area at the boundary of the monomer droplets and aqueous medium can be achieved, and the monomer can be effectively supplied to the polymerization based on diffusion. In this case, the effect of the homogenizer achieved is about the same as the effect achieved through the aforementioned ultrasonic treatment.

As described above, emulsion copolymerization of tetrafluoroethylene and other optional monomers is done after introducing the perfluorocarbon monomer having a sulfonic acid type functional group to the aqueous medium, and conditions used for the above-mentioned emulsion

copolymerization are not especially limited and conditions commonly used for this purpose can be used effectively in this case as well.

For the perfluorocarbon monomer having a sulfonic acid type functional group used in the present invention is not especially limited and known monomers can be used in this case as well. As a suitable monomer, fluoro vinyl compounds shown in the following general formula

$$CF_2{=}CF\text{-}(OCF_2CFX)_l\text{-}(O)_q\text{-}(CF_2)_n\text{-}(CF_2CFX')_m\text{-}A$$

(Wherein, l is 0-3, m is 0-3, n is 0-12 and q is either 0 or 1, and X is either -F or $-CF_3$, X' is either -F or $-CF_3$, and A is a sulfonic acid type functional group) can be mentioned. From the standpoint of availability, it is desirable when X and X' are $-CF_3$, l is either 0 or 1, m is 0, n is 0-8, q is either 0 or 1 and A is $-SO_2F$ from the standpoint of the copolymerization reaction, etc. As typical desirable examples of the above-mentioned fluoro vinyl compound,

$CF_2{=}CFO(CF_2)_{1\sim8}SO_2F$,

$CF_2{=}CFOCF_2CF(CF_3)O(CF_2)_{1\sim8}SO_2F$,

$CF_2{=}CF(CF_2)_{0\sim8}SO_2F$,

$CF_2{=}CF(OCF_2CF(CF_3))_{1\sim5}SO_2F$

etc. can be mentioned.

In the present invention, emulsion copolymerization is carried out for tetrafluoroethylene and the above-mentioned perfluorocarbon monomer having a sulfonic acid type functional group in an aqueous medium, and in this case, two or more different types of perfluorocarbon monomers having a sulfonic acid type functional group can be used, and furthermore, two or more different types of other components, for example, perfluorocarbon monomers containing a carboxylic acid type functional group, divinyl monomers such as $CF_2{=}CFORf$ (Rf is a perfluoroalkyl group with 1-10 carbon atoms) and $CF_2{=}CF\text{-}CF{=}CF_2$, and $CF_2{=}CFO(CF_2)_{1\text{ to }4}OCF{=}CF_2$ can be used in combination as well. However, the purpose of the

present invention is to produce a perfluorocarbon polymer copolymerized with a high proportion of a perfluorocarbon monomer having a sulfonic acid type functional group based on emulsion copolymerization in an aqueous medium, it is desirable when selection is made for the mixing ratio of the above-mentioned monomers in order to produce a perfluorocarbon polymer having a copolymerization ratio of the aforementioned perfluorocarbon monomer having a sulfonic acid type functional group of at least 20 wt%. It is further desirable when selection is made so as to produce a perfluorocarbon polymer having a copolymerization ratio of the aforementioned perfluorocarbon monomer having a sulfonic acid type functional group in the range of 25 to 60 wt%.

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When the perfluorocarbon polymer having a sulfonic acid type functional group of the present invention is used as an ion-exchange film, the ion-exchange capacity of the polymer can be selected over a wide range of 0.5 to 2.0 milliequivalents/gram dry resin, and when the conditions described below is utilized, the molecular weight of the copolymer produced can be increased even when the ion-exchange capacity is increased; thus, a reduction in mechanical properties and wear resistance of the copolymer does not occur. The ion-exchange capacity varies depending on the type of copolymer used and from the standpoint of mechanical properties and electrochemical properties of the polymer used as an ion-exchange resin, at least 0.7 milliequivalents/gram dry resin is desirable and at least 0.8 milliequivalents/gram dry resin is further desirable. Furthermore, the molecular weight of the perfluorocarbon polymer having a sulfonic acid type functional group produced in the present invention is important in relation to the mechanical properties and film formability of the ion-exchange film, and at least 150°C in terms of the value of TQ is suitable, and in the range of 170 to 340°C, and 180 to 280°C is further desirable.

In the specification of the present invention, the term "TQ" is defined as follows. The temperature that shows a volume flow velocity of 100 mm^3/sec having an influence on the molecular weight of the copolymer is defined as TQ. In this case, the volume flow velocity is shown in the units of the mm^3/sec of the polymer as melting is performed for the copolymer from an orifice with a diameter of 1 mm and a length of 2 mm at a constant temperature and under a pressure of 30 kg/cm^2. Furthermore, "the ion-exchange capacity" was obtained as shown below. In other words, an H-type cationic ion exchange film is stored in 1N HCl at 60°C for 5 hours so that complete conversion to H-type can be achieved, and a thorough washing was subsequently performed with water to prevent residual HCl. Then, 0.5 g of the above-mentioned H-type film was placed in a solution produced by adding 25 ml of water to 25 ml of 0.1N NaOH for 2 days at room temperature. Subsequently, the film was removed and a reverse titration was done for the amount of the NaOH in the solution with 0.1N HCl.

In the present invention, it is desirable when the copolymerization reaction of a functional group monomer such as sulfonic acid type monomer and tetrafluoroethylene at a weight ratio of the aqueous medium/functional monomer of 20/1 or below, preferably, 10/1 or below. When the amount of aqueous medium used is too high, the copolymer reaction rate is reduced and a long time is required to produce a high copolymer yield. Furthermore, when the amount of the aqueous medium used is too high, a polymer with a high molecular weight cannot be achieved when used as an high ion-exchange material. Furthermore, when an excess amount of the aqueous medium is used, a large-scale reaction device is required, or workability becomes complicated due to separation and recovery of the copolymer.

Furthermore, it is desirable when a copolymerization reaction pressure of at least 2 kg/cm^2 is used in the present invention. When the copolymerization reaction pressure is too low, it is difficult to maintain the copolymerization reaction rate at an adequate level and production of a copolymer with a high molecular weight is difficult. On the other hand, when the copolymerization reaction pressure is too low, the ion-exchange capacity of the copolymer

produced becomes too high and reduction in mechanical strength and ion-exchange capacity is likely to increase due to an increase in high water absorption. Furthermore, it is desirable when the copolymerization reaction pressure used in this case is 50 kg/cm^2 or below from the standpoint of reactor used or workability. It is possible to use a copolymerization reaction pressure of above the above-mentioned value, but an additional advantage cannot be achieved. Therefore, it is desirable when the copolymerization reaction pressure is selected from a range of 2 to 50 kg/cm^2, preferably, 4-30 kg/cm^2.

The aforementioned polymerization reaction, etc. are not especially limited in the copolymerization reaction of the present invention and selection can be made from a wide range. For example, the optimum value of the copolymerization reaction temperature is determined by the type of polymerization initiator used and the reaction molar ratio, etc., and in general, too high a temperature or too low a temperature is a disadvantage; thus, the temperature is selected to be in the range of 20 to 90°C, preferably, 30 to 80°C.

For the polymerization initiator used in the present invention, a material that exhibits high activity at the aforementioned suitable reaction temperature is desirable. For example, it is possible to use highly active ionizing radiation at a temperature below room temperature, but in general, use of azo compounds and peroxide compounds are further desirable from the standpoint of industrial application. For examples of the polymerization initiators used effectively in the present invention, diacyl peroxides such as disuccinic acid peroxide, benzoyl peroxide, lauroyl peroxide and dipentafluoropropionyl peroxide, azo compounds such as 2,2'-azobis(2-amidinopropane)hydrochlorate and azobisisobutylonitrile, peroxide esters such as t-butylperoxyisobutylate, and t-butylperoxy-pivalate, peroxy dicarbonate such as di-isopropylperoxy dicarbonate and di-2-ethylhexylperoxy dicarbonate, hydroperoxides such as di-isopropyl benzene hydroperoxide, inorganic peroxides such as potassium persulfate and ammonium persulfate, and redox thereof can be mentioned.

In the present invention, the concentration of the polymerization initiator used is in the range of 0.0001 to 3 wt%, preferably, in the range of 0.0001 to 2 wt%, for the total monomer. It is possible to increase the molecular weight of the copolymer produced by reducing the concentration of the initiator and retention of high ion-exchange capacity is made possible. When the concentration of the initiator is too high, the molecular weight is likely to be reduced, and production of a copolymer with a high ion-exchange capacity and high molecular weight is less likely to occur.

Furthermore, a variety of surfactants, dispersants, buffers, molecular weight modifiers, etc. commonly used for emulsion copolymerization in an aqueous medium can be used in this case as well. Furthermore, inert organic solvents known as a Freon type solvents such as fluoride or hydrogen fluoride type saturated hydrocarbons may be added as long as the copolymerization reaction of the present invention is not inhibited and chain transfer ratio is low.

In the present invention, the reaction is performed in such a manner that the concentration of the copolymer produced of 40

wt% or below, preferably, 30 wt% or below, can be achieved. When the concentration is too high, increase in non-uniformity of the copolymer composition and dispersing failure of the latex pose problems.

The sulfonic acid type perfluorocarbon polymer of the present invention can be formed into a film by an appropriate means. For example, the functional group is converted to a sulfonic acid group by means of hydrolysis reaction and the hydrolysis reaction can be carried out before or after the film formation. In general, it is desirable when the hydrolysis reaction is carried out after film formation. A variety of means can be used for film formation, and for example, known methods such as hot-melt molding, latex molding, and injection molding after dissolving in an appropriate solution can be used. Furthermore, lamination with a film having a different ion-exchange capacity or a film having a different functional group such as carboxylic acid group to

form two or more layers can be done. Furthermore, reinforcement can be provided with a material such as cloth, fibers, or a non-woven fabric.

The ion-exchange film made of the sulfonic acid type perfluorocarbon polymer of the present invention with excellent properties can be used for a variety of applications. For example, the film can be used effectively as a barrier membrane of diffusion dialysis, electrolytic reduction, and fuel battery in a field where corrosion resistance is required. In particular, when used as a cation selective barrier film of alkali electrolyte, high performance can be achieved when laminated with a carboxylic acid type film. For example, in the case of so-called two-cell tank in which the anode and cathode are separated by the above-mentioned cationic ion-exchange film to provide the structure of an anodic cell and cathodic cell, an alkali chloride solution is supplied to the anodic cell and electrolysis is performed and an alkali hydroxide is obtained from the cathodic cell, and long-term stable production of sodium hydroxide with a high concentration of at least 30% can be achieved with high current efficiency and low tank voltage when an electrolysis reaction is carried out at a current density of 5 to 50 A/cm^2 using a sodium chloride solution with a concentration of at least 2N.

The present invention is further explained in specific terms with working examples below, but needless to say, the present invention is not limited to these working examples.

Working example 1

0.2 g of $C_8F_{17}CO2NH4$, 0.50 g of Na_2HPO_4-$12H_2O$ and 0.29 g of NaH_2PO_4 were dissolved in 100 g of deionized water and 20 g of CF_2=$CFOCF_2CF(CF_3)O(CF_2)_2SO_2F$ was further added.

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Subsequently, emulsification treatment was performed for 10 minutes at a rate of 16500 rpm using an Ace Homogenizer AM7 of Nippon Seiki Co., Ltd. When a measurement was performed for the mean particle diameter of the monomer droplet dispersed in the solution by a particle analyzer PA101 of Union Giken Co., Ltd., 0.56 u was obtained. After the emulsification

treatment, 26 mg of $(NH_4)_2S_2O_8$ was added to the above-mentioned solution, and charged to a stainless steel pressure resistant reactor with 0.2 liter capacity, a thorough degassing was performed with liquid nitrogen, and the temperature was adjusted to 57°C, and then, 11 kg/cm^2 of tetrafluoroethylene was charged and the pressure was retained constant. After 8 hours, purging was performed for the non-reacting tetrafluoroethylene and the polymerization was completed, the latex produced was collected, washed, and dried to produce 21 g of copolymer. The ion-exchange capacity of the aforementioned copolymer was 1.12 meq/g. When press molding was performed for the aforementioned copolymer at a temperature of 250°C, a film with a high strength was produced, and when a hydrolysis reaction was performed with a 25% NaOH solution, a sulfonic acid type ion-exchange film was produced.

When a polymerization reaction and post treatments were performed in the same manner without application of ultrasonic wave [sic], ion-exchange capacity was absent in the copolymer produced.

Working example 2

The emulsification treatment time was changed to 90 minutes and when an emulsification treatment was performed as in the case of working example 1, the diameter of the monomer droplets in the solution was 0.46 μ. When polymerization reaction and post treatment were performed with the aforementioned solution as in the case of working example 1, the ion-exchange capacity achieved was 1.09 meq/g dry resin.

Working example 3

The pressure of tetrafluoroethylene was changed to 8 Kg/cm^2 and when a polymerization reaction and post treatments were performed as in the case of working example 1, the ion-exchange capacity achieved was 1.29 meq/g dry resin.

[Effect of the invention]

According to the method of the present invention, it is possible to effectively and smoothly disperse a perfluorocarbon monomer having a sulfonic acid type functional group in an aqueous medium.

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